

SCIENCE FOR GLASS PRODUCTION

UDC 666.1

BOROSILICATE GLASS STRUCTURE WITH RARE-EARTH-METAL CATIONS SUBSTITUTED FOR SODIUM CATIONS

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IR and RS spectroscopy are used to study the effect of substituting barium and calcium for the sodium cation on the structure of sodium borosilicate glass with the composition $0.25\text{Na}_2\text{O}$; $0.25\text{B}_2\text{O}_3$; 0.5SiO_2 . Analysis of the recorded spectra showed that the substitution of the alkali-metal cations Ba^{2+} and Ca^{2+} for the Na^+ cation results in breaking of B–O–B and Si–O–Si bridges, as a result of which the fraction of oxygen end atoms increases and the degree of polymerization of the glass decreases.

Key words: spectroscopy, structure, borosilicate glasses.

Matrices based on borosilicate glasses with different composition, which have the advantages of high radiation resistance and simple fabrication technology, are now widely used to immobilize radwastes [1]. Even though these glasses have long been used as a matrix material, the search for optimal compositions remains unresolved and requires continued study of the structure and properties of borosilicate glasses with a wide spectrum of compositions.

The objective of the present work was to study the effect of substituting calcium and barium for the sodium cation on the structure of sodium borosilicate glass with the composition (mole fraction) $0.25\text{Na}_2\text{O}$; $0.25\text{B}_2\text{O}_3$; 0.5SiO_2 . The structure of glass with this composition has been studied in detail experimentally in [2, 3] and theoretically in [4]. It has been established that the boron atoms in this glass can occupy ternary and quaternary coordination, the former are mainly flat symmetric triangles $\text{B}\text{O}_{3/2}$ (O — oxygen bridge atom) in which all oxygen atoms are bridge atoms. The fraction of asymmetric triangles $\text{B}\text{O}_{2/2}\text{O}^-$ is small but measurable experimentally. The silicate component of the network of this glass is represented as Q^4 , Q^3 and, possibly, in very small amounts Q^2 units (Q^n — silicon-oxygen tetrahedron with n oxygen bridge atoms). Thermodynamic modeling shows that the fraction of different types of structural units in glasses with the compositions studied is as follows [4]:

$\text{B}\text{O}_{4/2}(\text{B}_4) — 0.152$;
 $\text{B}\text{O}_{3/2}(\text{B}_3) — 0.173$;
 $\text{B}\text{O}_{2/2}\text{O}^-(\text{B}_{3-}) — 0.009$;
 $\text{Q}^4(\text{Si}\text{O}_{4/2}) — 0.326$;
 $\text{Q}^3(\text{Si}\text{O}_{3/2}\text{O}^-) — 0.336$;
 $\text{Q}^2(\text{Si}\text{O}_{2/2}\text{OO}_2^-) — 0.002$.

On the whole it is evident that the distribution of the sodium ions between the silicon- and boron-containing structural units is approximately proportional to the value $K = \text{SiO}_2/\text{B}_2\text{O}_3$ (2 : 1). The sodium ions compensate the charge of the borate tetrahedral and oxygen end atoms belonging to the silicate structural units.

EXPERIMENTAL PART

Two series of glasses were synthesized and studied in this work. In the first series, calcium cations were gradually substituted for sodium cations, while in the second series barium cations were substituted for the sodium cations. The glasses were synthesized from reagents: analytically pure SiO_2 , ultrapure B_2O_3 , and chemically pure CaO , BaO , and Na_2CO_3 . The initial reagents taken in the appropriate proportions were carefully mixed with alcohol in a porcelain mortar, dried at temperature 100–150°C, and melted in a platinum crucible in an electric furnace with a nichrome heater at temperature 1200°C or with silicon carbide heaters at temperature 1350°C (glass with high calcium and barium content). The melting operation was conducted for 3–10 h, depending on the composition, to complete homogenization of

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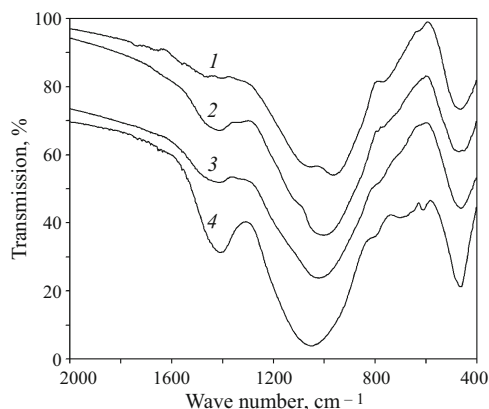


Fig. 1. Infrared spectra of calcium-containing glass: 1) N4; 2) N3Cl; 3) N2C2; 4) N1C3.

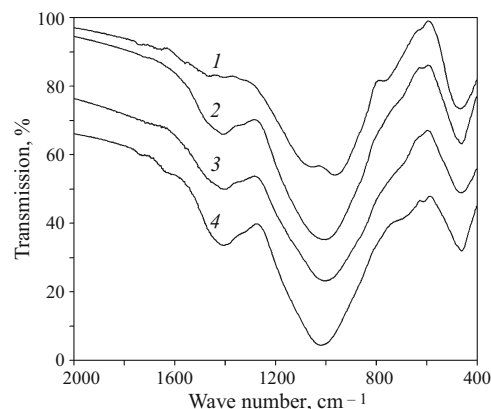


Fig. 2. Infrared spectra of barium-containing glass: 1) N4; 2) N3Bl; 3) N2B2; 4) N1B3.

the melt. The melt was poured into a collapsible metal mold with an 8 mm in diameter cylindrical cavity. All samples were uniform, transparent, glass disks approximately 3–5 mm high and 8 mm in diameter. The compositions of the glasses synthesized are presented in Table 1.

Raman light-scattering and IR spectroscopy were used to study the structural features of the glasses obtained. The material for IR-spectroscopy was obtained in thin sections from a sample, mixed with KBr, ground, and pressed into a transparent pellet. The IR transmission spectra were recorded with a NEXUS single-beam IR Fourier spectrometer. The RS spectra were recorded with an apparatus based on a DFS-24 dual monochromator [5]. An LTI-701 solid-state pulsed laser (wavelength $\lambda = 532$ nm, average power $\langle P \rangle = 1$ W, pulse repetition frequency $\nu = 8.7$ kHz, pulse duration on an electro-optic shutter $\tau = 2$ μ sec) was used to excite the spectra. The spectra were recorded in a 180° geometry. The spectral width of the slit did not exceed 7 cm^{-1} in any experiment. A FÉU-79 photomultiplier operating in the photon counting mode served as a detector for the scattered radiation.

RESULTS AND DISCUSSION

An intense absorption band peaking near $900 - 1100$ cm^{-1} dominates the spectrum of the initial N4 sodium glass

(Figs. 1 and 2). This band has a complex shape and is a superposition of two components – an absorption band peaking near 970 cm^{-1} and a line near 1065 cm^{-1} . In addition, three additional and weaker bands peaking near 460 , 780 , and 1420 cm^{-1} can be identified in the spectrum. When calcium and barium are substituted for sodium, the shape of the dominant absorption band changes and the band peak shifts into the high-frequency region (see Figs. 1 and 2). At the same time, the intensity of the band peaking at 1420 cm^{-1} increases somewhat, a small band peaking near 715 cm^{-1} appears, and the line at 780 cm^{-1} shifts by approximately 20 cm^{-1} into the high-frequency region.

The band peaking near 460 cm^{-1} is due to deformation vibrations of the Si–O–Si bridges, the band near $780 - 800$ cm^{-1} is related with deformation vibrations of the Si–O[−] end groupings, and the band peaking near 970 cm^{-1} attests to the presence of BO_4 tetrahedra in the structure of the glass [6]. The 1065 cm^{-1} band in the spectrum of the sodium glass is related with the asymmetric stretching vibrations of the Si–O–Si bonds and the shift of its peak is due to a change of the degree of polymerization of the glass structure [7]. The absorption bands peaking near 715 and 1420 cm^{-1} are associated with different vibrational modes of the planar BO_3 triangles [8].

RS SPECTROSCOPY

The RS spectra of the experimental glasses are displayed in Figures 3 and 4. These spectra were interpreted using the accepted decomposition into low- and high-frequency parts. A wide band peaking near 600 cm^{-1} dominates in the low-frequency region of the RS spectrum of the initial N4 glass; this band is a sum of two close-lying bands peaking near 580 and 635 cm^{-1} . When barium is substituted for the sodium cation (see Fig. 3) the shape of the spectral contour in the frequency region changes appreciably. The position of the peak of the low-frequency component of the fundamental band shifts to low frequencies, down to 540 cm^{-1} , and at the same

TABLE 1. Chemical Composition of the Synthesized Glasses

Sample	Composition, mole fraction				
	Na_2O	BaO	CaO	B_2O_3	SiO_2
N4	0.250			0.25	0.5
N3C1	0.188		0.062	0.25	0.5
N2C2	0.125		0.125	0.25	0.5
N1C3	0.062		0.188	0.25	0.5
N3B1	0.188	0.062		0.25	0.5
N2B2	0.125	0.125		0.25	0.5
N1B3	0.062	0.188		0.25	0.5

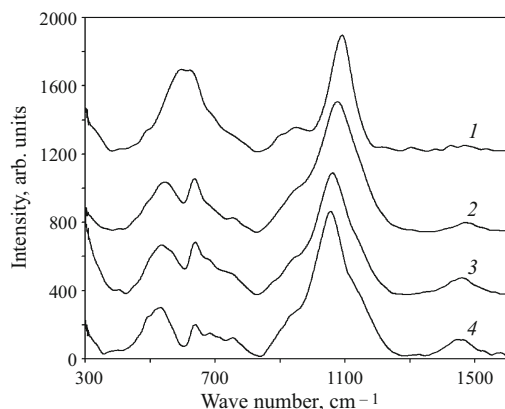


Fig. 3. Raman scattering spectra of barium-containing glasses: 1) N4; 2) N3B1; 3) N2B2; 4) N1B3.

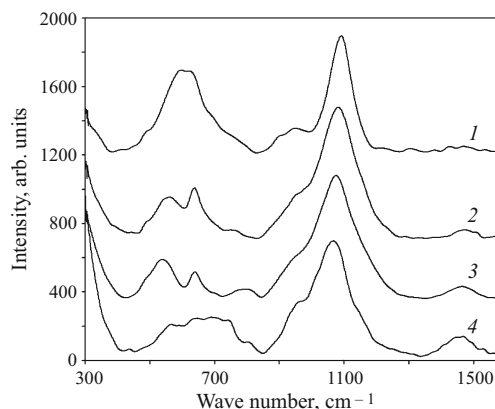


Fig. 4. Raman scattering spectra of calcium-containing glasses: 1) N4; 2) N3C1; 3) N2C2; 4) N1C3.

time the intensity of the high-frequency component (635 cm^{-1} band) decreases. Similar changes are observed in the spectra of the calcium-containing glasses (see Fig. 4). An appreciable difference between the spectra of barium- and calcium-containing glasses appears only for compositions where the alkali-earth cations predominate appreciably (spectra of the glasses N1B3 and N1C3).

The band peaking near $560\text{--}600\text{ cm}^{-1}$ is related with the symmetric stretching and deformation vibrations of the Si–O–Si(B) bridge bonds. The shift of its peak attests to a change of the type of bridge bond. According to the data in [9, 10] the 635 cm^{-1} band is due to symmetric stretching vibrations of ring-type metaborate anions. At the same time, according to the data in [11] this line can also be attributed to the vibrations of B–O–B(Si) bonds in mixed borosilicate (danburite- and reedmergnerite-like) rings consisting of SiO_4 and BO_4 tetrahedra, represented in the ratios 2 : 1 and 3 : 1, respectively. For this reason, the intensity decrease occurring for this band when calcium and barium are substituted for sodium can attest to a decrease of the boron atom fraction in the tetrahedral coordination as well as to a decrease of the metaborate anions $\text{B}_3\text{O}_6^{3-}$ in the structure.

Bands at 910, 960, and 1100 cm^{-1} are observed in the high-frequency part of the RS spectrum of the initial sodium glass, the 1100 cm^{-1} band being the strongest. As barium and calcium cations are systematically substituted for sodium the peak of the dominant band shifts into the low-frequency part of the spectrum and the integral intensity of this band increases. Likewise, the peak of the 960 cm^{-1} band shifts by a small amount and its integral intensity increases. At the same time, bands peaking near $1470\text{--}1480\text{ cm}^{-1}$ appear in the RS spectra of the experimental glasses and their intensities increase.

It is known that the bands in the region $900\text{--}1200\text{ cm}^{-1}$ are due to stretching vibrations of the end groupings of silicon-oxygen tetrahedra Q^n with different ratio of the bridge and non-bridge oxygen atoms (n is the number of oxygen bridge atoms) [12]. For this reason the lines at 910, 960, and

1100 cm^{-1} were assigned to stretching vibrations of the oxygen end atoms in the SiO_4 tetrahedra with one, two, and three bridge bonds (Q^1 , Q^2 , and Q^3 units), respectively. The intensities of the characteristic bands of Q^2 -type structural units increase when calcium and barium are substituted for sodium.

The bands in the range from 1200 and 1500 cm^{-1} are well-known to be associated with the vibrations of trigonal borate units with a different number of end groupings. The band peaking in the range $1470\text{--}1480\text{ cm}^{-1}$ was interpreted as a manifestation of the vibrations of non-bridge B–O[−] bonds in a metaborate triangle $\text{BO}_{2/2}\text{O}^-$ with one non-bridge oxygen atom [13]. For this reason, the growth of the intensity of this line when an alkali-earth metal (calcium and barium) is substituted for sodium cations is due to an increase in the fraction of the structural units $\text{BO}_{2/2}\text{O}^-$ with one non-bridge oxygen atom.

CONCLUSIONS

The character of the change in the spectra indicates that when alkali-earth metals (Ca and Ba) are substituted for sodium in sodium borosilicate glass with the composition (mole fraction) $0.25\text{Na}_2\text{O}$; $0.25\text{B}_2\text{O}_3$; 0.5SiO_2 the following changes occur:

- the fraction of Si–O–Si and B–O–B bonds decreases because these bonds break with oxygen end atoms being formed mainly in the silicate structural units Q^2 ;
- the fraction of boron atoms in the low-coordination form (III B) increases and, at the same time, the fraction of metaborate triangles $\text{BO}_{2/2}\text{O}^-$ containing non-bridge oxygen atoms increases substantially.

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